In-Situ Characterization of Additives Governing Copper Electrodeposition

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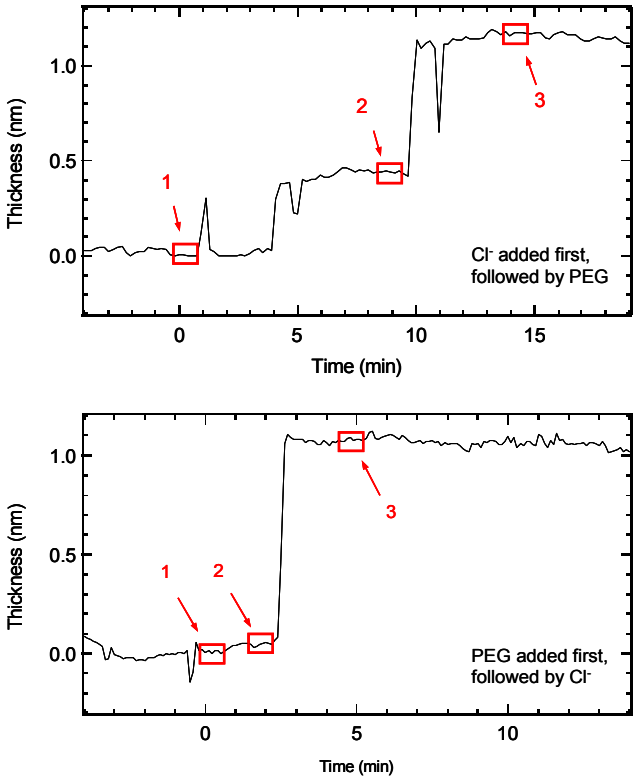
NIST researchers adapt a commercially available spectroscopic ellipsometer to evaluate the effect of additives on metal substrates in liquid-based environments to mimic the electrolytic plating baths used in the industry.

One of the critical issues facing the microelectronic/semiconductor industry is the robust fabrication of "on-chip" interconnections (wiring) between transistors and related devices. Due to its lower resistivity and superior electromigration characteristics, copper has replaced aluminum as the metal of choice for such interconnects. Interconnections are formed by electrodepositing copper into lithographically-defined sub-micrometer wide features (trenches and vias). The feature filling process occurs by superconformal or "bottom-up" growth that derives from a competition between electrolyte additives, such as inhibitors and catalysts, for available surface sites. A representative additive package to plating baths contains polyethylene glycol (PEG), chloride (Cl^-) and sulfonate-terminated disulfides such as $Na_2[SO_3(CH_2)_3S]_2$ (SPS). Inhibition is provided by PEG/Cl^- while disruption of the PEG species by SPS/Cl^- leads to acceleration of the metal deposition. Incorrectly formulated baths can lead to uncontrolled electrodeposition, resulting in faulty interconnect creation and poor device performance. The PEG/Cl^- system was studies to more fully characterize synergies between bath components and probe the utility of spectroscopic ellipsometry (SE) for the *in situ* evaluation of electrodeposition.

Spectroscopic ellipsometry is a non-destructive optical technique capable of measuring optical characteristics of a surface, and is routinely used in the semiconductor industry to evaluate wafer quality.

The formation of a film upon the addition of PEG and Cl^- was observed, and the results indicate that *in-situ* dynamic SE can accurately measure film thickness with better than 0.1 nm accuracy under certain conditions.



Ellipsometrically-determined model thickness trace of the layer formed on a copper substrate in the presence of the additives of PEG and Cl^- in an electrolytic bath at a plating potential. In the top graph baseline was established at "1", Cl^- added after 4 minutes and measured at "2", PEG was added at 10 minutes and measured at "3".

In the second graph the baseline was established at 1, PEG added after 1 minute and measured at "2", Cl^- added after 2 minutes and measured at "3".

The results show the presence of Cl^- is necessary for the formation of a film, but a film eventually forms regardless of additive order. The adsorbed PEG film thickness is approximately 0.5 nm, consistent with a single layer of helically-wound PEG. Additional studies on gold and silver substrates established that chelation of copper ions is not necessary for film formation.

Studies on the three-component PEG/Cl^-/SPS system are planned to build on the insights gained from the PEG/Cl^- system. Additionally, the use of other materials such as ruthenium as substrates for copper electrodeposition applications will be examined.

M.L. Walker, L.J. Richter, and T.P. Moffat, *"In-Situ Ellipsometric Study of PEG/Cl- Co-adsorption on Cu, Ag and Au"*, submitted to J. Electrochemical Soc.